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(54) Energy polymerizable composition containing organometallic initiators.

(57) An energy polymerizable composition and process therefore, comprising a cationically polymerizable material and a catalytically effective amount of an ionic salt of an organometallic complex cation as polymerization initiator, said ionic salt of an organometallic complex cation being capable of adding an intermediate strength nucleophile or upon photolysis capable of liberating at least one coordination site, said metal in said organometallic complex cation being selected from elements of Periodic Groups IVB, VB, VIB, VIIB, and VIIIB are disclosed. Certain of the organometallic metallic polymerization initiators are novel cationic salts.

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Description  
Energy Polymerizable Compositions  
Containing Organometallic Initiators

Technical Field

5 The present invention relates to a process for the polymerization of cationically-sensitive materials employing as polymerization initiator a certain class of ionic organometallic compounds. In another aspect, it relates to polymerizable compositions containing 10 cationically-sensitive materials and organometallic complex compounds. In a further aspect, it relates to certain organometallic polymerization initiators.

Background Art

15 The prior art describes various processes for the initiation of cationic polymerization, particularly the polymerization of epoxy materials. It is known to cure epoxy materials by use of curing additives such as polybasic anhydrides, organic peroxides, and quinone. It is further known that a metalocene, such as ferrocene, can be 20 used as a curing accelerator for epoxy materials and is described in U.S. Patent No. 3,705,129. U.S. Patent Nos. 3,709,861 and 3,714,006 describe the use of cyclopentadienylmanganese tricarbonyl for the acceleration of the light-catalyzed reaction between polyepoxides and acid 25 anhydrides or polymercaptans. U.S. Patent No. 3,867,354 discloses the use of bis- and tris-salicylic acid complexes of chromium(III) to catalyze the reaction between epoxides and carboxylic acids, and U.S. Patent No. 4,237,242 relates to the use of transition metal complexes (chromium, 30 manganese, iron, etc.) of acetylacetonate type ligands to accelerate the thermally initiated reaction of carboxylic acid group-containing polymers with polyepoxides. Each of the above-mentioned patents teaches the acceleration of the reaction between polyepoxides and polyfunctional curing additives, but they do not teach the polymerization of

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epoxide group-containing compositions not containing a curing additive.

5 The polymerization of cationically-polymerizable materials, specifically epoxide group-containing materials, in the absence of curing additives is, however, well known. Among such processes are those in which the polymerization catalyst (also called sensitizer or initiator) is (1) a radiation-sensitive onium salt of a Lewis acid (e.g. diazonium salts as are described in U.S. Patent No. 3,794,576 and U.S. Patent No. 4,000,274; halonium salts as are disclosed in U.S. Patent No. 4,026,795; and the onium salts of Group VIA elements, particularly the sulfonium salts, as are disclosed in U.S. Patent No. 4,059,400); (2) a dicarbonyl chelate compound of a Group IIIA-VA element as is disclosed in U.S. Patent No. 4,086,083; (3) a silver salt which is used for the polymerization of tetrahydrofuran as is described by Woodhouse, et al., *J. Am. Chem. Soc.*, 100, 996 (1978); and (4) titanocene dichloride which is used for the polymerization of epichlorohydrin and 20 2-chloroethylvinyl ether as is described by Merrifield, et al., *J. Polym. Sci., Chem. Ed.*, 10, 2833 (1972) and *ibid.*, 14, 1547 (1976). Compositions containing the above-mentioned catalysts are unsatisfactory because without the addition of optical sensitizers they are 25 limited to ultraviolet radiation for polymerization. Furthermore, the dicarbonyl chelates are moisture sensitive and the titanocene dichloride requires a co-catalyst.

Disclosure of the Invention

30 The present invention provides a process for the polymerization of cationically-sensitive materials utilizing as catalyst a cationic compound which is a salt of an organometallic complex cation. By selection of the metal and ligands in the organometallic complex and the counterion used, the relative thermal stability and wave- 35 length of sensitivity (from 200 to 600 nm) can be adapted for various applications.



L<sup>4</sup> represents none, or 1 to 6 bridging ligands containing o-electrons that can be the same or different ligand selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of acting as a bridging ligand contributing 2 to 24  $\pi$ -electrons to the valence shells of two or more metal atoms M<sup>a</sup>, M<sup>b</sup>, M<sup>c</sup>, or M<sup>d</sup> simultaneously;

10 L<sup>5</sup> represents none, or 1 to 12 bridging ligands contributing an even number of o-electrons that can be the same or different selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 o-electrons to the valence shells of two or more metal atoms M<sup>a</sup>, M<sup>b</sup>, M<sup>c</sup>, or M<sup>d</sup> simultaneously;

15 L<sup>6</sup> represents none or 1 to 12 bridging ligands contributing 1, 2, 3, or 4 o-electrons to the valence shells of two or more metal atoms M<sup>a</sup>, M<sup>b</sup>, M<sup>c</sup>, or M<sup>d</sup> simultaneously;

20 with the proviso that the total electronic charge contributed to M<sup>a</sup>, M<sup>b</sup>, M<sup>c</sup>, and M<sup>d</sup> by the ligands L<sup>1a</sup>, L<sup>2a</sup>, L<sup>3a</sup>, L<sup>1b</sup>, L<sup>2b</sup>, L<sup>1c</sup>, L<sup>2c</sup>, L<sup>3c</sup>, L<sup>1d</sup>, L<sup>2d</sup>, L<sup>3d</sup>, L<sup>4</sup>, L<sup>5</sup>, and L<sup>6</sup> plus the sum of ionic charge on M<sup>a</sup>, M<sup>b</sup>, M<sup>c</sup>, and M<sup>d</sup> results in a residual net positive charge of e to the complex;

25 e is an integer having a value of 1, 2, or 3, the residual electrical charge of the complex cation;

X is a halogen-containing complex anion of a metal or metalloids;

30 f is an integer of 1 to 3, the number of complex anions required to neutralize the charge e on the complex cation; and

g, h, j, and k independently are 0 or 1, with at least one of them being equal to 1.

35 In a preferred composition of the invention, the salts of the organometallic cation have the formula:



wherein

M<sup>a</sup> represents a metal selected from elements of the Periodic Groups IVB, VB, VIB, VIIA, VIII, and VIIIB;

L<sup>7</sup> represents none, one or two ligands contributing

5  $\pi$ -electrons that can be the same or different ligand selected from the same group of ligands from which L<sup>1a</sup>, L<sup>1b</sup>, L<sup>1c</sup>, and L<sup>1d</sup> ligands of Formula I is selected;

L<sup>8</sup> represents none or 1 to 6 ligands contributing an even number of o-electrons that can be the same or different ligand selected from the same group of ligands from which L<sup>2a</sup>, L<sup>2b</sup>, L<sup>2c</sup>, and L<sup>2d</sup> ligands of Formula I is selected;

15 with the proviso that the total electronic charge contributed to M<sup>a</sup> by L<sup>7</sup> and L<sup>8</sup> plus the ionic charge on M<sup>a</sup> results in a residual net positive charge of e to the complex; and e, f, and X have the same definition as given in Formula I.

In a most preferred composition of the invention, the salts of the organometallic cation are novel and have the formula:



wherein

MP represents a metal selected from Cr, Mn, W, Mo, Re, Ru, and Co;

25 L<sup>9</sup> represents 1 or 3 ligands contributing  $\pi$ -electrons that can be the same or different ligand selected from substituted and unsubstituted n<sup>3</sup>-allyl, n<sup>3</sup>-cyclopentadienyl, and n<sup>7</sup>-cycloheptatrienyl and n<sup>6</sup>-aromatic compounds selected from n<sup>6</sup>-benzene and substituted n<sup>6</sup>-benzene compounds and compounds having 2 to 4 fused rings each capable of contributing 3 to 8  $\pi$ -electrons to the valence shell of MP;

30 L<sup>10</sup> represents none or 1 to 3 ligands contributing an even number of o-electrons that can be the same or different ligand selected from carbon monoxide or nitrosonium;



- sulfur, oxygen, phosphorus, arsenic, selenium, antimony, and tellurium, in addition to the metal atom, following loss of zero, one, or two hydrogens, the polydentate compounds preferably forming with the metal,  $M^2$ ,  $M^3$ ,  $M^4$ ,  $M^5$ , and  $M^6$ , a 4-, 5-, or 6-membered saturated or unsaturated ring. Examples of suitable monodentate compounds or groups are carbon monoxide, carbon sulfide, carbon selenide, carbon telluride, alcohols such as ethanol, butanol, and phenol; nitrates (i.e.,  $NO^+$ ); compounds of Group VA elements such as ammonia, phosphine, trimethylamine, trimethylphosphine, triphenylamine, triphenylphosphine, triphenylarsine, triphenylstibine, tributylphosphite, isocyanides such as phenylisocyanide, butylisocyanide; carbene groups such as ethoxymethylcarbene, dithiomethoxycarbene; alkyldienes such as methylidene, ethylidene; suitable polydentate compounds or groups include 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylarsino)ethane, bis(diphenylphosphino)methane, ethylenediamine, propylenediamine, diethylenetriamine, 1,3-diaocyanatopropane, and hydrotetrapyrzolyborate; the hydroxycarboxylic acids such as glycolic acid, lactic acid, salicylic acid; polyhydric phenols such as catechol and 2,2'-dihydroxybiphenyl; hydroxyamines such as ethanolamine, propanolamine, and carbamate, dibenzylidithiocarbamate; xanthates such as ethyl xanthate, phenyl xanthate; the dithiolenes such as bis(perfluoromethyl)-1,2-dithiolene; aminocarboxylic acids such as alanine, glycine and  $\alpha$ -aminobenzoic acid; dicarbonylic diamides such as oxalamide, biuret; diketones such as 2,4-pentanedione; hydroxyketones such as 2-hydroxyacetophenone;  $\alpha$ -hydroxyamines such as salicylaldoxime; ketoximes such as benzil oxime; and glyoximes such as dimethylglyoxime. Other suitable groups are the inorganic groups such as, for example,  $CN^-$ ,  $SCN^-$ ,  $P^-$ ,  $OH^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ , and  $H^-$  and the organic groups such as, for example, acetyl, formyl, benzoyl, etc. As mentioned before, the

acrylate), poly( $\alpha$ -methylstyrene), polyvinylcarbazole, and polymethylphenylsiloxanes; the cyclopentadiene group in poly(vinylcyclopentadiene), poly( $n^6$ -cyclopentadiene); the pyridine group in poly(vinylpyridine), etc. Polymers having a weight average molecular weight up to 1,000,000 or more can be used. It is preferable that 5 to 50 percent of the unsaturated or aromatic groups present in the polymer be combined with metallic cations.

Each of the ligands 1a, 1b, 1c, 1d, and 1f can be substituted by groups that do not interfere with the complexing of the ligand with the metal atom or which do not reduce the solubility of the ligand to the extent that complexing with the metal atom does not take place.

Examples of substituting groups, all of which preferably have less than 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron, include hydrocarbyl groups such as methyl, ethyl, butyl, decyl, tetradecyl, phenyl, benzyl, allyl, benzylidene, ethynyl, and ethynyl; hydrocarbyloxy groups such as methoxy, butoxy, and phenoxy; hydrocarbylmercapto groups such as methylmercapto (thiomethyl), phenylmercapto (thiophenyl); hydrocarbylthiocarbonyl such as methoxy-

carbonyl and phenylthiocarbonyl; hydrocarbylcarbonyl such as formyl, isopropyl, and benzoyl; hydrocarbylcarboxylate such as acetate, benzoate, and cyclohexanecarboxylate; hydrocarbylcarbamate,  $\alpha$ - $\beta$ -acetamide, benzamide, azo; benzyl; halo,  $\alpha$ - $\beta$ -chloro, bromo, iodo, fluoro, and fluoro; hydrazyl; cyano; nitro; nitroso; azo; dimethylamino; diphenylphosphine, diphenylarsine, dimethylstibine; trimethylamine; tributyl-

amine; methylamine; ethylamine; and trimethylolol; condensed rings such as benzene, cyclopentadiene, naphthalene, indene, and the like.

Ligands 1a, 1b, 1c, 1d, and 1f in Formula I, and 1g in Formula II are provided by monodentate and polydentate compounds preferably containing up to about 30 carbon atoms and up to 10 hetero atoms selected from nitrogen,

ligand can be a unit of a polymer, for example the amino group in poly(ethyleneimine); the phosphino group in poly-(4-vinylphenylphosphine); the carboxylic acid group in poly(acrylic acid); and the isonitrile group in poly-(4-vinylphenylisonitrile).

Suitable radicals L<sup>3</sup>, L<sup>2b</sup>, L<sup>3c</sup>, and L<sup>3d</sup> in Formula I include any group having in its structure an atom with an unshared electron. Suitable groups can contain any number of carbon atoms and hetero atoms but preferably contain less than 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron. Examples of such groups are hydrocarbyl groups such as methyl, ethyl, propyl, butyl, dodecyl, phenyl, tosyl, etc.; unsaturated hydrocarbyl groups such as vinyl, allyl, butenyl, cyclohexenyl; the hydrocarbyl derivatives of a Group IVA element such as trimethylgermanium, triphenylsilane, and trimethylaluminum, etc.; and organic groups such as formyl, acetyl, propionyl, acryloyl, octadecoyl, benzoyl, cinnamoyl, allyl, malonyl, o-phthaloyl.

Ligand L<sup>4</sup> in Formula I is provided by any symmetric or polymeric compound having an accessible unsaturated group, such as an acetylenic, -CEC- group or an aromatic group which have accessible  $\pi$ -electrons in conjunction of the total molecular weight of the compound.

Illustrative of ligand L<sup>4</sup> are the linear and cyclic diene and acetylenic compounds preferably having less than 60 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, boron, antimony, tellurium, silicon, germanium, and tin, such as for example, acetylene, methylacetylene, diacetylene, butadiene, 1,2-dimethylacetylene, 1,3-cyclohexadiene, cyclopentadiene, and 1,4-cyclohexadiene;  $\eta^3$ -allyl,  $\eta^3$ -pentenyl, norbornadiene,  $\eta^5$ -cyclohexadienyl,  $\eta^5$ -cycloheptatriene,  $\eta^5$ -cyclooctatetraene, and substituted and unsubstituted carbocyclic and heterocyclic aromatic ligands having up to 25 rings and up to 100 carbon atoms

and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, boron, antimony, tellurium, silicon, germanium, and tin, such as, for example,  $\eta^5$ -cyclopentadienyl,  $\eta^6$ -benzene,  $\eta^6$ -mesitylene,  $\eta^6$ -hexamethylbenzene,  $\eta^6$ -fluorene,  $\eta^6$ -naphthalene,  $\eta^6$ -anthracene,  $\eta^6$ -chrysene,  $\eta^6$ -pyrene,  $\eta^7$ -cycloheptatrienyl,  $\eta^7$ -triphenylmethane,  $\eta^5$ -pyrrole,  $\eta^5$ -thiophene,  $\eta^5$ -furan,  $\eta^5$ -pyridine,  $\eta^6$ -picoline,  $\eta^6$ -quinoline,  $\eta^6$ -benzopyran,  $\eta^6$ -thiochrome,  $\eta^6$ -benzoxazine,  $\eta^6$ -indole,  $\eta^6$ -acridine,  $\eta^6$ -carbazole,  $\eta^6$ -(1,2,3,4,4a,12a)- $\eta^6$ -(7,8,9,10,10a,10b)chrysene,  $\eta^6$ -triphenylene,  $\eta^6$ ,  $\eta^6$ -paracyclophane,  $\eta^6$ ,  $\eta^6$ -1,4-diphenylbutane,  $\eta^6$ -silabenzene,  $\eta^6$ -arabenzene,  $\eta^6$ -tetrabenzene,  $\eta^6$ -2,4,6-triphenylphosphabenzene,  $\eta^5$ -selenophene,  $\eta^6$ -dibenzostannepine,  $\eta^5$ -tellurophene,  $\eta^6$ -phenothiazine,  $\eta^6$ -selenanthrene,  $\eta^6$ -phenoxaphosphine,  $\eta^6$ -phenoxazine,  $\eta^6$ -phenatellurazine, and  $\eta^6$ -1-phenylborabenzene. Other suitable aromatic compounds can be found by consulting any of many chemical handbooks.

Each of the ligands L<sup>4</sup> can be substituted by groups that do not interfere with the complexing of the ligand with the metal atom or which do not reduce the solubility of the ligand to the extent that complexing with the metal atom does not take place. Examples of substituting groups, all of which preferably have less than 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron, include hydrocarbyl groups such as methyl, ethyl, butyl, dodecyl, tetradecyl, phenyl, benzyl, allyl, benzylidene, ethenyl, and ethynyl; hydrocarbyloxy groups such as methoxy, butoxy, and phenoxy; hydrocarbylmercapto groups such as methylmercapto (thiomethoxy), phenylmercapto (thiophenoxy); hydrocarbylthiocarbonyl such as methoxycarbonyl and phenoxycarbonyl; hydrocarbylcarbonyl such as formyl, acetyl, and benzoyl; hydrocarbylcarbonyloxy such as acetoxy, benzoxy, and cyclohexanecarbonyloxy; hydrocarbylcarbonamido, e.g., acetamido, benzamido; azo; furyl; halo,

o, o', chloro, iodo, bromo, and fluoro, hydroxy, cyano, nitro, nitroso, azo, dimethylamino, diphenylphosphino, diphenylarsino, diphenylstibino, trimethylgermane, tributyltin, methylseleno, ethyltelluro, and trimethylsiloxy; 5 condensed rings such as benzo, cyclopenta, naphtho, indenyl, and the like.

Ligand L<sup>5</sup> is provided by monodentate and polydentate compounds preferably containing up to about 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, selenium, arsenic, phosphorus, tellurium, antimony, and boron. Examples of suitable monodentate compounds or groups are carbon monoxide, carbon sulfide, carbon selenide, carbon telluride, alcohols such as ethanol, butanol, and phenyl nitroethanol (i.e., HO<sup>+</sup>); compounds of 15 Group VA elements such as triphenylamine, triphenylphosphine, triphenylarsine, triphenylstibine, isocyanides such as isocyanide, suitable polydentate compounds or groups include 1,3-bis(diphenylphosphino)ethane, 1,3-bis(diphenylarsino)ethane, bis(diphenylphosphino)methane, ethylenediamine, propylenediamine, diethylenetriamine, 1,3-diaminopropane, and hydriotripyrazolylborate; the hydriotripyrazolyl borate such as glycolic acid, lactic acid, salicylic acid, polyaromatic phenols such as catechol and 2,3'-dihydroxybiphenyl, hydroxyacids such as ethanediol, 25 propylenediol, and 2-methylpropanediol; dithiocarbamates such as diethylthiocarbamate, diisopropylthiocarbamate, xanthates such as ethyl xanthate, phenyl xanthate; the dithiolenes such as bis(phenylthio)ethane, 1,2-dithiolane; aminoarboic acids such as alanine, glycine and o-aminobenzoic acid; dicarboxylic diamines such as oxalimide, biuret; diketones such as 2,6-pyridinedione; hydroxyketones such as 2-hydroxyacetophenone; o-hydroxyketones such as salicylformate; ketones such as benzil oxime; and glyoximes such as dimethylglyoxime. Other suitable groups are the inorganic groups such as, for example, CN<sup>-</sup>, SCN<sup>-</sup>, F<sup>-</sup>, OH<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and S<sup>2-</sup> and the organic groups such as, for example, acetoxy, formyl, benzoyloxy, etc.

15 Group VA elements such as triphenylamine, triphenylphosphine, triphenylarsine, triphenylstibine, isocyanides such as isocyanide, suitable polydentate compounds or groups include 1,3-bis(diphenylphosphino)ethane, 1,3-bis(diphenylarsino)ethane, bis(diphenylphosphino)methane, ethylenediamine, propylenediamine, diethylenetriamine, 1,3-diaminopropane, and hydriotripyrazolylborate; the hydriotripyrazolyl borate such as glycolic acid, lactic acid, salicylic acid, polyaromatic phenols such as catechol and 2,3'-dihydroxybiphenyl, hydroxyacids such as ethanediol, 25 propylenediol, and 2-methylpropanediol; dithiocarbamates such as diethylthiocarbamate, diisopropylthiocarbamate, xanthates such as ethyl xanthate, phenyl xanthate; the dithiolenes such as bis(phenylthio)ethane, 1,2-dithiolane; aminoarboic acids such as alanine, glycine and o-aminobenzoic acid; dicarboxylic diamines such as oxalimide, biuret; diketones such as 2,6-pyridinedione; hydroxyketones such as 2-hydroxyacetophenone; o-hydroxyketones such as salicylformate; ketones such as benzil oxime; and glyoximes such as dimethylglyoxime. Other suitable groups are the inorganic groups such as, for example, CN<sup>-</sup>, SCN<sup>-</sup>, F<sup>-</sup>, OH<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and S<sup>2-</sup> and the organic groups such as, for example, acetoxy, formyl, benzoyloxy, etc.

35 Group VA elements such as triphenylamine, triphenylphosphine, triphenylarsine, triphenylstibine, isocyanides such as isocyanide, suitable polydentate compounds or groups include 1,3-bis(diphenylphosphino)ethane, 1,3-bis(diphenylarsino)ethane, bis(diphenylphosphino)methane, ethylenediamine, propylenediamine, diethylenetriamine, 1,3-diaminopropane, and hydriotripyrazolylborate; the hydriotripyrazolyl borate such as glycolic acid, lactic acid, salicylic acid, polyaromatic phenols such as catechol and 2,3'-dihydroxybiphenyl, hydroxyacids such as ethanediol, 25 propylenediol, and 2-methylpropanediol; dithiocarbamates such as diethylthiocarbamate, diisopropylthiocarbamate, xanthates such as ethyl xanthate, phenyl xanthate; the dithiolenes such as bis(phenylthio)ethane, 1,2-dithiolane; aminoarboic acids such as alanine, glycine and o-aminobenzoic acid; dicarboxylic diamines such as oxalimide, biuret; diketones such as 2,6-pyridinedione; hydroxyketones such as 2-hydroxyacetophenone; o-hydroxyketones such as salicylformate; ketones such as benzil oxime; and glyoximes such as dimethylglyoxime. Other suitable groups are the inorganic groups such as, for example, CN<sup>-</sup>, SCN<sup>-</sup>, F<sup>-</sup>, OH<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and S<sup>2-</sup> and the organic groups such as, for example, acetoxy, formyl, benzoyloxy, etc.

Suitable radical L<sup>6</sup> in Formula I includes any group having in its structure an atom with two or more unpaired electrons. Suitable groups can contain any number of carbon atoms and hetero atoms but preferably contain 5 less than 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron. Examples of such groups are hydrocarbyl groups such as methenyl, ethenyl, propenyl, hexenyl, 10 dodecenyl, methynyl, and carbide.

Suitable anions, X, in Formulas I and II, of use as the counterion in the ionic salts of the organometallic complex cation is the preferred radiation-sensitive compositions of the invention are those in which X has the formula DQ<sub>2</sub>, wherein D is a metal from Groups IB to VIII or a metal or metalloid from Groups IIA to VA of the Periodic Chart of Elements, O is a halogen atom, and r is an integer having a value of 1 to 6. Preferably, the metals are copper, zinc, titanium, vanadium, chromium, 20 manganese, iron, cobalt, or nickel and the metalloids preferably are boron, aluminum, antimony, tin, arsenic, and phosphorus. Preferably, the halogen, O, of Formula II, is chlorine or fluorine. Illustrative of suitable anions are BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, FeCl<sub>4</sub><sup>-</sup>, SnCl<sub>3</sub><sup>-</sup>, SbF<sub>5</sub><sup>-</sup>, AlF<sub>6</sub><sup>-</sup>, GaCl<sub>4</sub><sup>-</sup>, InF<sub>4</sub><sup>-</sup>, TiF<sub>6</sub><sup>-</sup>, ZrF<sub>6</sub><sup>-</sup>, etc. Preferably, the anions are BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, SbF<sub>5</sub>OH<sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, and SbCl<sub>6</sub><sup>-</sup>. Most preferably, the anions are AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, and SbF<sub>5</sub>OH<sup>-</sup>. Some of the organometallic complex salts having these three anions are novel and all of these salts provide compositions of the invention that are relatively more active toward polymeriza- 30 tion on exposure to energy than are salts having other anions.

Ligand L<sup>9</sup> in Formula III is provided by linear and cyclic olefinic compounds formally described as having lost a hydride or a proton alpha to a double bond from a saturated carbon and having less than 10 carbon atoms and no heteroatoms, such as for example n<sup>3</sup>-allyl, n<sup>3</sup>-butenyl, n<sup>3</sup>-pentenyl, n<sup>3</sup>-hexenyl, n<sup>3</sup>-heptenyl, n<sup>3</sup>-octenyl, 35 and cyclic olefinic compounds formally described as having lost a hydride or a proton alpha to a double bond from a saturated carbon and having less than 10 carbon atoms and no heteroatoms, such as for example n<sup>3</sup>-allyl, n<sup>3</sup>-butenyl, n<sup>3</sup>-pentenyl, n<sup>3</sup>-hexenyl, n<sup>3</sup>-heptenyl, n<sup>3</sup>-octenyl.

different substituents from methyl, ethyl, propyl, isopropyl, methoxy, ethoxy, hydroxy, nitro, chloro, bromo, amino, and N,N-dimethylamino on the phenyl ring in the 2,3, 2,4, or 3,4 positions.

There are restrictions on the total sum of electrons donated by the ligands,  $L_1, L_2, L_3, L_4, L_5, L_6, L_7, L_8, L_9, L_{10}, L_{11}, L_{12}, L_{13}, L_{14}, L_{15}, L_{16}, L_{17}, L_{18}, L_{19}, L_{20}, L_{21}, L_{22}, L_{23}, L_{24}, L_{25}, L_{26}, L_{27}, L_{28}, L_{29}, L_{30}$ , and the valence electrons possessed by the metal,  $M^0, M^1, M^2, M^3, M^4, M^5, M^6, M^7, M^8, M^9, M^{10}, M^{11}, M^{12}, M^{13}, M^{14}, M^{15}, M^{16}, M^{17}, M^{18}, M^{19}, M^{20}, M^{21}, M^{22}, M^{23}, M^{24}, M^{25}, M^{26}, M^{27}, M^{28}, M^{29}, M^{30}$ , and  $M^P$ . For most complex compounds not involving intramolecular metal-metal bonding, this sum is governed by the "eighteen electron rule" [see J. Chem. Ed. 46, 811 (1969)]. This rule is sometimes called the "noble gas rule", "the effective number rule", or the "rare gas rule". This rule states that the most stable organometallic compounds tend to be those compounds in which the sum of the electrons donated by the ligands and the metal is eighteen. Those skilled in the art, however, know that there are exceptions to this rule and that organometallic complex compounds having a sum of 16, 17, 19, and 20 electrons are also known. Therefore, ionic salts of organometallic complex cations not including intramolecular metal-metal bonding are described by Formulas 1, 11, and 111 in which complexed metal  $M^0, M^1, M^2, M^3, M^4, M^5, M^6, M^7, M^8, M^9, M^{10}, M^{11}, M^{12}, M^{13}, M^{14}, M^{15}, M^{16}, M^{17}, M^{18}, M^{19}, M^{20}, M^{21}, M^{22}, M^{23}, M^{24}, M^{25}, M^{26}, M^{27}, M^{28}, M^{29}, M^{30}$  have a total sum of 16, 17, 18, 19, or 20 electrons in the valence shell and a residual net positive charge of 3 are included within the scope of the invention.

For complex compounds described in Formula 1 in which intramolecular metal-metal bonding exists serious departure from the "eighteen electron rule" can occur. It has been proposed [J. Am. Chem. Soc. 100, 5305 (1978)] the departure from the "eighteen electron rule" in these transition metal complexes is due to the metal-metal interactions destabilizing the metal p orbitals to an extent to cause them to be unavailable for ligand bonding. Hence, rather than count electrons around each metal separately in a metal cluster, cluster valence electrons (CVE) are counted. A dinuclear complex,  $M_2P_4$ , is seen to

$n^3$ -nonenyl,  $n^3$ -decenyl,  $n^3$ -cyclobutenyl,  $n^3$ -cyclopentenyl,  $n^3$ -cyclohexenyl,  $n^3$ -cycloheptenyl,  $n^3$ -cyclooctenyl,  $n^3$ -cyclononenyl,  $n^3$ -cyclodecenyl,  $n^5$ -methylcyclopentadienyl,  $n^5$ -cyclopentadienyl,  $n^5$ -pentamethylcyclopentadienyl,  $n^5$ -cyclopentadienyl, and  $n^7$ -cycloheptatrienyl (it being understood that both the  $n^5$ -cyclopentadienyl and the  $n^7$ -cycloheptatrienyl ligand may be formally described as an aromatic ligand) and aromatic ligands having up to 4 rings and up to 24 carbon atoms and up to 2 heteroatoms selected from nitrogen, oxygen, and sulfur, such as, for example,

$n^6$ -toluene,  $n^6$ -ethylbenzene,  $n^6$ -isopropylbenzene,  $n^6$ -propylbenzene,  $n^6$ -t-butylbenzene,  $n^6$ -m-xylene,  $n^6$ -o-xylene,  $n^6$ -p-xylene,  $n^6$ -1,3,5-trimethylbenzene (mesitylene),  $n^6$ -1,2,4-trimethylbenzene,  $n^6$ -1,3,5-trimethylbenzene,  $n^6$ -1,2,3,4-tetramethylbenzene,  $n^6$ -1,2,3,5-tetramethylbenzene,  $n^6$ -1,2,4,5-tetramethylbenzene (durane),  $n^6$ -pentamethylbenzene,  $n^6$ -hexamethylbenzene,  $n^6$ -phenol,  $n^6$ -thiophenol,  $n^6$ -anisole,  $n^6$ -thioanisole,  $n^6$ -aniline,  $n^6$ -N,N-dimethylaniline,  $n^6$ -diphenylamine,  $n^6$ -diphenylmethane,  $n^6$ -triphenylmethane,  $n^6$ -chlorobenzene,  $n^6$ -bromobenzene,  $n^6$ -fluorobenzene,  $n^6$ -cyanobenzene,  $n^6$ -nitrobenzene,  $n^6$ -fluorene,  $n^6$ -carbazole,  $n^6$ -biphenyl,  $n^6$ -triphenylene,  $n^6$ -naphthalene,  $n^6$ -anthracene,  $n^6$ -phenanthracene,  $n^6$ -pyrene,  $n^6$ -chrysene,  $n^6$ -tetralin,  $n^6$ -ethoxybenzene,  $n^6$ -benzoic acid,  $n^6$ -quinoline,  $n^6$ -isoquinoline,  $n^6$ -indole,  $n^6$ -benzimidazole,  $n^6$ -1,2-benzopyrazole,  $n^6$ -benzothiazole,  $n^6$ -benzoxazole,  $n^6$ -indan,  $n^6$ -paracyclophane,  $n^6$ -1,4-diphenylbutane,  $n^6$ -paracyclophane,  $n^6$ -1,4-diphenylbutane, poly( $n^6$ -styrene),

poly( $n^6$ -vinylcarbazole), poly( $n^6$ -methylphenylsiloxane), poly( $n^6$ -1,2,3,4,4a,9a-9-(phenylmethylidene)fluorene, and  $n^6$ -1,2,3,4,4a,9a-9-(3-phenyl-2-propenylidene)fluorene. The latter two ligands may be mono-substituted by groups selected from methyl, ethyl, propyl, isopropyl, methoxy, ethoxy, hydroxy, nitro, chloro, bromo, amino, and N,N-dimethylamino on the phenyl ring. Also, the latter two ligands may be disubstituted by groups that may be same or

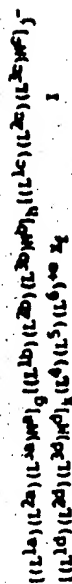
have 34 CVEs, a trinuclear complex,  $M^A_3M^B_3C_6$ , 48 CVEs, and a tetranuclear complex,  $M^A_4M^B_4C_8$ , having tetrahedron, butterfly, and square planar geometry is seen to have 60, 62, or 64 CVEs, respectively. Those skilled in the art, however, know that there are exceptions to this electron counting method and that organometallic complex cluster compounds having a sum of 42, 44, 46, 50 CVEs for a trinuclear complex and 58 CVEs for a tetranuclear complex are also known. Therefore, ionic salts of di, tri, or tetranuclear organometallic complex cations are described by Formula 1 in which the complexed metal cluster,  $M^A_nM^B_nC_n$ , or  $M^A_nM^B_nC_n$  has a total sum of 34, 42, 44, 46, 48, 50, or 58, 60, 62, 64 CVEs in the valence shell, respectively, and a residual net positive charge of 1, 2, or 3 are included within the scope of this invention.

Suitable organometallic complex ionic salts described by Formulas 1, II, III of use in the compositions of the invention are those salts that upon application of sufficient energy, either thermal or electromagnetic radiation having a wavelength from about 200 to 600 nm, will generate an active species capable of initiating cationic polymerization. The level of cationic activity will, of course, depend on the choice of metal, ligands, and counterions in the salt.

Suitable ionic salts that are activated by heat to initiate cationic polymerization are those that will add an intermediate strength nucleophile such as substituted or unsubstituted trialkyl- and triarylphosphines (preferably triphenylphosphine), trialkyl- and triarylphosphites, pyridines, and anilines. Examples of such compounds are described in Tetrahedron 34, 3047 (1978) and "Carbonium Ions" 5, Chapter 37, 1976, Wiley-Interscience, New York. These reviews contain references to the experimental procedures used to determine if a particular compound will add such a nucleophile.

Suitable ionic salts that are activated by electromagnetic radiation to initiate cationic polymeriza-

tion are those that upon photolysis liberate at least one coordination site on the metal. The ability to liberate at least one coordination site upon photolysis can be verified by doing a ligand exchange experiment. In such an experiment, the compound



is photolyzed in the presence of a potential entering ligand L (L can be of the L<sup>1</sup> or L<sup>2</sup> types). That L has indeed added or exchanged with at least one ligand L<sup>1</sup> to L<sup>20</sup> of formula I can be determined by any number of analytical techniques. It is particularly convenient for this determination to use some spectroscopic technique to monitor the reaction before, during, and after photolysis. If L or at least one of the L<sup>20</sup>, L<sup>21</sup>, L<sup>22</sup>, L<sup>23</sup>, or L<sup>24</sup> ligands is carbon monoxide, then infrared spectroscopy is a well suited technique to monitor the reaction. Observation UV/visible or NMR spectroscopy can be employed. The spectrum before photolysis can be compared with that taken after completion of the reaction to determine if the suspected ligand substituted product is present. A more rigorous method would involve isolation of the photoproduct after completion of the reaction and use of an analytical technique such as elemental analysis to verify that L has indeed entered the coordination sphere of the metal. The proper conditions under which the ligand exchange experiment should be carried out, i.e., organometallic ionic salt concentration, identity of the entering ligand, entering ligand concentration, choice of solvent, irradiation wavelength, irradiation time, light source, light source intensity, reaction vessel, presence or absence of oxygen, analysis technique, etc., must be adjusted by the experimentalist for the particular system under study. Examples of the conditions which have been used to study ligand exchange reactions are contained in "Organometallic

Photochemistry", 1979, Academic Press, New York, and references therein, and in Inorg. Chem., 19, 3007 (1980).

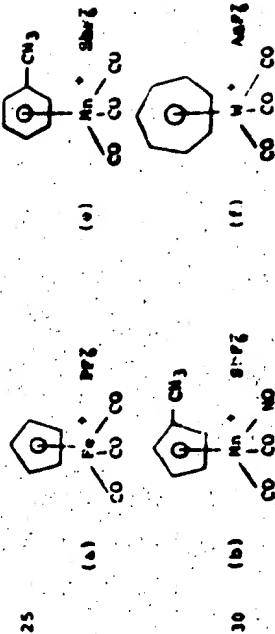
Examples of suitable salts of organometallic complex cations useful in the composition of the invention include the following (proposed structures of typical compounds are shown at the end of the list):

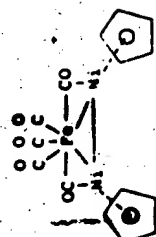
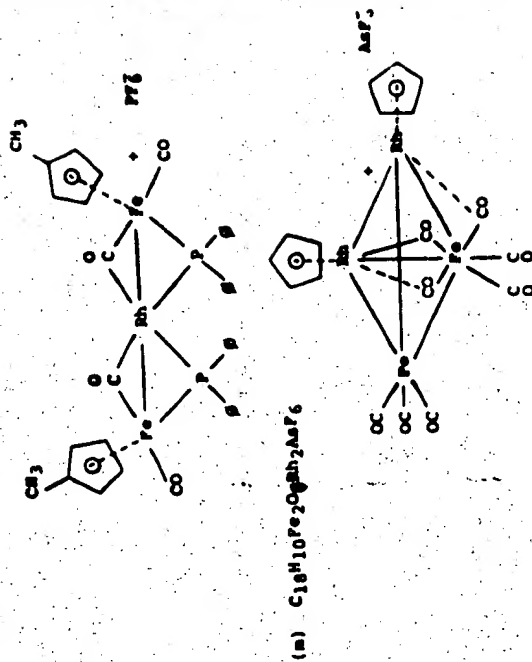
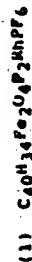
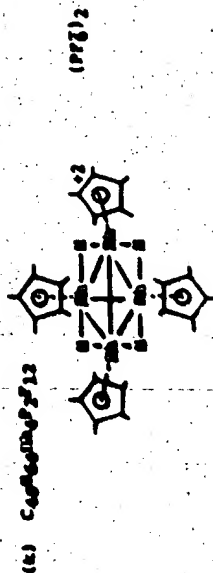
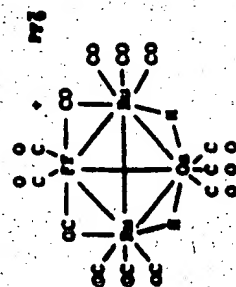
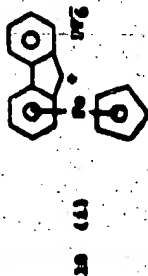
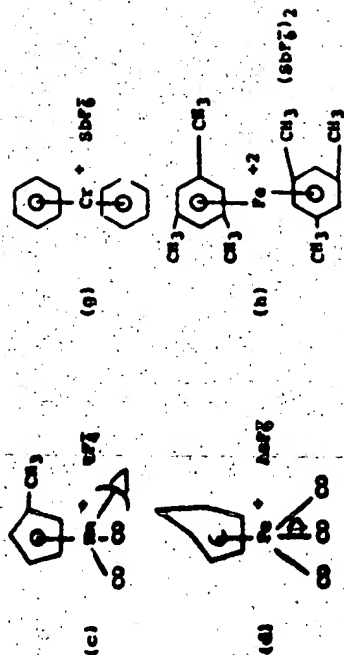
- ( $\eta^5$ -cyclopentadienyl)tricarbonyliron(1+) hexafluorophosphate (a)
- ( $\eta^5$ -cyclopentadienyl)dicarbonylthiocarbonyliron(1+)
- ( $\eta^5$ -cyclopentadienyl)iron(1+)
- ( $\eta^5$ -cyclopentadienyl)tricarbonylbis(triphenylstibine)iron(1+)
- ( $\eta^5$ -cyclopentadienyl)tricarbonylruthenium(1+)
- tetrachloroferrate
- ( $\eta^5$ -cyclopentadienyl)dicarbonyltriphenylstibineiron(1+)
- hexafluoroantimonate
- ( $\eta^5$ -methylcyclopentadienyl)dicarbonylnitrosylmanganese(1+)
- hexafluoroantimonate (b)
- ( $\eta^5$ -methylcyclopentadienyl)( $\eta^3$ -allyl)dicarbonylmanganese(1+)
- tetrafluoroborate (c)
- ( $\eta^5$ -cyclopentadienyl)tetracarbonylmolybdenum(1+)
- hexafluorophosphate
- ( $\eta^5$ -pentadienyl)tricarbonyliron(1+) tetrafluoroborate
- ( $\eta^5$ -cyclohexadienyl)tricarbonyliron(1+) hexafluoroarsenate (d)
- ( $\eta^5$ -cyclohexadienyl)(ethylidene)carbonyltriphenylphosphineiron(1+) tetrafluoroborate
- ( $\eta^5$ -cyclopentadienyl)(ethoxymethylcarbene)carbonyltriphenylphosphineiron(1+) tetrafluoroborate
- ( $\eta^5$ -cyclopentadienyl)(dithiomethoxycarbene)-dicarbonyliron(1+) hexafluorophosphate
- ( $\eta^5$ -cyclopentadienyl)dicarbonylmethylisonitrileiron(1+)
- hexafluoroarsenate
- bis( $\eta^5$ -cyclopentadienyl)( $\eta^2$ -ethylene)( $\sigma$ -methyl)tungsten(1+)
- hexafluorophosphate
- ( $\eta^6$ -cycloheptatriene)tricarbonylmanganese(1+) hexafluoroantimonate (e)
- ( $\eta^6$ -mesitylene)tricarbonylrhenium(1+) hexafluoroantimonate

- ( $\eta^7$ -cycloheptatrienyl)tricarbonylchromium(1+)
- hexafluorophosphate
- ( $\eta^7$ -cycloheptatrienyl)tricarbonyltungsten(1+)
- hexafluoroarsenate (f)
- 5 ( $\eta^5$ -cyclopentadienyl)( $\eta^2$ -1-pentene)dicarbonyliron(1+)
- tetrafluoroborate
- ( $\eta^6$ -benzene)( $\eta^5$ -cyclopentadienyl)iron(1+)
- hexafluorophosphate
- ( $\eta^6$ -mesitylene)( $\eta^5$ -cyclopentadienyl)iron(1+)
- 10 tetrafluoroborate
- ( $\eta^6$ -naphthalene)( $\eta^5$ -cyclopentadienyl)iron(1+)
- hexafluoroantimonate
- ( $\eta^6$ -acetophenone)( $\eta^5$ -methylcyclopentadienyl)iron(1+)
- hexafluoroarsenate
- 15 bis( $\eta^5$ -cyclopentadienyl)cobalt(1+) hexafluorophosphate
- bis( $\eta^5$ -cyclopentadienyl)iron(1+) hexafluoroantimonate
- bis( $\eta^5$ -chlorocyclopentadienyl)nickel(1+) hexafluorophosphate
- bis( $\eta^6$ -benzene)rhodium(1+) hexafluoroantimonate (g)
- bis( $\eta^6$ -hexamethylbenzene)cobalt(2+) hexafluoroarsenate
- 20 bis( $\eta^6$ -hexamethylbenzene)nickel(2+) hexafluoroantimonate
- tetracarbonyltriphenylphosphinecobalt(1+) hexafluorophosphate
- tricarbonylbis(triphenylphosphine)iridium(1+) hexafluorophosphate
- 25 ( $\eta^3$ -allyl)pentacarbonylchromium(1+) tetrafluoroborate
- pentacarbonylnitrosylmolybdenum(1+) hexafluorophosphate
- ( $\eta^3$ -allyl)tetracarbonyliron(1+) hexafluoroantimonate
- hexacarbonylrhodium(1+) hexafluoroantimonate
- bis( $\eta^6$ -mesitylene)iron(2+) hexafluoroantimonate (h)
- 30 bis( $\eta^6$ -hexamethylbenzene)manganese(1+) tetrafluoroborate
- bis( $\eta^6$ -mesitylene)vanadium(1+) hexafluorophosphate
- ( $\eta^7$ -cycloheptatrienyl)( $\eta^5$ -cyclopentadienyl)manganese(1+)
- hexafluoroarsenate
- ( $\eta^8$ -cyclooctatetraenyl)( $\eta^5$ -cyclopentadienyl)chromium(1+)
- 35 hexafluorophosphate
- ( $\eta^6$ -fluorene)( $\eta^5$ -cyclopentadienyl)iron(1+) hexafluorophosphate (i)

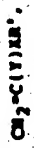
- ( $\eta^6$ -1-phenylborabenzene)( $\eta^5$ -cyclopentadienyl)cobalt(1+)  
hexafluorophosphate  
( $\eta^5$ -cyclopentadienyl)( $\eta^5$ -N-methylpyrrolyl)iron(1+)  
hexafluorophosphate
- 5 ( $\eta^6$ -2,3,4,5-tetramethoxybenzene)( $\eta^5$ -cyclopentadienyl)-  
iron(1+) hexafluoroarsenate  
[( $\eta^6$ -1,2,3,4,5,6)( $\eta^6$ -7,8,9,10,11,12)biphenyl]bis( $\eta^5$ -cyclo-  
pentadienyl)diron(2+) tetrafluoroborate  
[( $\eta^6$ -1,2,3,4,4a,9a)( $\eta^6$ -5,6,7,8,8a,5a)fluorene]bis( $\eta^5$ -cyclo-  
pentadienyl)diron(2+) hexafluorophosphate  
10 [( $\eta^6$ -1,2,3,4,4a,9a)( $\eta^6$ -5,6,7,8,8a,5a)fluorene]bis-  
( $\eta^5$ -benzene)diron(4+) hexafluorophosphate  
[( $\eta^6$ -1,2,3,4,4a,12a)( $\eta^6$ -7,8,9,10,10a,6a)chrysene]-  
bis( $\eta^5$ -benzene)dichromium(2+) hexafluoroantimonate
- 15 dicarbonyl[bis(diphenylphosphino)ethane]bis( $\eta^5$ -cyclopenta-  
dienyl)diron(1+) hexafluorophosphate  
tetra[( $\eta^5$ -cyclopentadienyl)carbonyl]iron(1+) hexafluoro-  
phosphate  
tris[( $\eta^6$ -benzene)cobalt]dicarbonyl(1+) hexafluorophosphate  
20 tris( $\eta^5$ -cyclopentadienyl)dinickel(1+) hexafluorophosphate  
[( $\eta^6$ -1,2,29,18c,18a)( $\eta^6$ -7,8,8a,18i,18h,7a)( $\eta^6$ -13,14,-  
14a,10a,18b,12a)( $\eta^6$ -18c,18u,18v,18x,18y)-tripyrreno-  
(2,1,10,9,0,7-degph)]2,1',10',9',8',7'-naphgret:  
2,1',10',9',8',7'-xyza,b,c,d(trinaphthalene)tetra( $\eta^5$ -  
cyclopentadienyl)tetrairon(4+) hexafluoroantimonate  
25 [( $\eta^6$ -4,5,5a,28c,78b,3a)( $\eta^6$ -8a,8b,20d,22b,24c)-18,14h-  
dipyranol(3,4,5, gh: 3',4',5'-g'h')anthra(2',1',9':  
4,5,6'6',5',10'-4',5',6')dilequinol(2,1'-a2',1'-a1)-  
dipyrimidine]bis( $\eta^5$ -cyclopentadienyl)diron(2+)
- 30 hexafluoroantimonate  
[( $\eta^6$ -1,2,2,3a,13a)benzo(10,11)chrysene(2,3-d)(1,3)-  
disole]( $\eta^5$ -methylcyclopentadienyl)iron(1+)  
hexafluorophosphate  
[( $\eta^6$ -1,2,3,3a,16c,16b)( $\eta^6$ -9,10,11,11a,13c,8b)cycloocta-  
35 (1,2,3,4-det:5,6,7,8-d'e'e')diphenanthrene]bis( $\eta^5$ -  
acetyl)cyclopentadienyl)diron(2+) tetrafluoroborate  
bis[( $\eta^5$ -acetyl)cyclopentadienyl]iron(1+) tetrafluoroborate

- [( $\eta^6$ -1,2,2,4,4a,42a)( $\eta^6$ -16,17,18,19,19a,15a)( $\eta^6$ -30,31,32,  
32a,32b,29a)naphth(8',1',2':6,5,10)anthra(2,3-1)naphthn-  
(2'''',3''',6'',7'')indolo(2',3':5'6')naphth(2',3':6,5)-  
indolo(2,3-g)naphtho(2,3-1')benzo(1,2-a:4,5-a')dices-  
5 basole]tris( $\eta^5$ -cyclopentadienyl)triliron(3+) hexa-  
fluoroantimonate  
( $\eta^3$ -1-methyl-allyl)tricarbonyliron(1+) hexafluorophosphate  
( $\eta^3$ -1,3-dimethyl-allyl)tricarbonyliron(1+) hexachloro-  
antimonate  
10 [( $\eta^5$ -cyclopentadienyl)nickelmonocarbonyl]tricobalt(1+)  
hexafluorophosphate  
Di-( $\mu$ -carbonyl)tricarbonyl(dicarbonyliron)(hexacarbonyl)-  
hydrodiruthenium)- $\mu$ -hydro-osmium(2Fe-Ru)(Fe-Os)-  
(2Os-Ru)(Ru-Ru)(1+) hexafluorophosphate(1)  
15 Tetra- $\mu$ -hydrotetrakis[(1,2,3,4,5- $\eta$ )-1,2,3,4,5-pentamethyl-  
2,4-cyclopentadienyl-1-yl]-tetra-~~tetrahedry~~-rhodium-  
(+2) bis(hexafluorophosphate)(n)  
Bis( $\mu$ -diphenylphosphido- $\mu$ -carbonyl)- $\mu$ -methylcyclopentadienyl)-  
carbonyliron)rhodium(2Rh-Fe)(1+) hexafluorophosphate(1)  
20 Di- $\mu$ -carbonylpentacarbonyl- $\mu$ -carbonyldi- $\mu$ -cyclopentadienyl-  
dirhodium)diron(Fe-Fe)(4Fe-Rh)(Rh-Rh)(1+)  
hexafluoroarsenate(m)  
Di- $\mu$ -3-carbonyl)tricarbonylbis( $\mu$ -cyclopentadienyl)nickello)-  
iron(2Fe-Ni)(Ni-Ni)(1+) hexafluoroantimonate(n)





Cationically polymerizable materials that can be cured or polymerized by the compounds of this invention, using the latter in a catalytically effective amount, are those known to undergo cationic polymerization and include 1,2-, 1,3-, and 1,4-cyclic ethers (also designated as 1,2-,



where X is -O- or -NR<sup>n</sup>- (where R<sup>n</sup> is hydrogen or lower alkyl), R<sup>n</sup> is hydrocarbyl, hydrocarbylcarbonyl, haloalkylcarbonyl, or hydroxyhydrocarbyl when X is oxygen, or R<sup>n</sup> is hydrocarbyl, hydrocarbylcarbonyl, or hydrocarbylalkoxy when X is nitrogen, and Y is hydrogen, alkyl, aryl, or other hydrocarbyl, or R<sup>n</sup> (as hydrocarbylcarbonyl) and R<sup>n</sup> can be connected to form a 5- or 6-membered cyclic structure containing nitrogen as a hetero ring atom. The term "hydrocarbyl" is used herein in its usual sense to mean alkyl, alkenyl, aryl, cycloalkyl, cycloalkenyl, alkaryl, arylalkyl, and the like. In general, monomers of this type contain a vinyl group and are typified by vinyl alkyl ethers, such as vinyl methyl ether, vinyl ethyl ether, vinyl n-butyl ether, vinyl 2-chloroethyl ether, vinyl isobutyl ether, vinyl phenyl ether and vinyl 2-ethylhexyl ether, vinyl ethers of substituted aliphatic alcohols such as 1,4-di(ethenoxy)butane, vinyl 4-hydroxybutyl ether, and n-vinyl compounds such as n-vinyl-n-methyl octanesulfonamide and n-vinylpyrrolidone. A description of vinyl monomers and their use in preparing polymers is set forth in "Vinyl and Related Polymers," by Schildknecht, published by John Wiley & Sons, Inc., New York (1952).

Other cationically-sensitive monomers which can be polymerized in this invention include ethylenically unsaturated hydrocarbons such as isobutylene, 1,3-butadiene, isoprene, styrene, and divinylbenzene; cyclic formals such as trioxane, 1,3-dioxolane, 2-vinyl-1,3-dioxolane and 2-methyl-1,3-dioxolane; and cyclic siloxanes which can contain various groups attached to the silicon atom such as a hydrocarbon radical (alkyl, aryl, alkaryl), an alkenyl hydrocarbon radical (vinyl, allyl or acryloyloxy-alkyl), a halogenated hydrocarbon radical, a carbonyl-containing hydrocarbon radical or ester group, a cyanohydrocarbon radical, hydrogen, halogen or a hydroxy group. Representative cyclic siloxanes are

1,3-, and 1,4-epoxides), vinyl ethers, n-vinyl compounds, ethylenically unsaturated hydrocarbons, cyclic formals, and cyclic organosiloxanes. An extensive list of cationically polymerizable monomers which can be used in this invention are given in U.S. Patent Nos. 3,347,676 and 3,842,019.

The cyclic ethers which can be polymerized in accordance with this invention include those described in "Ring-Opening Polymerizations", Vol. 2, by Frisch and Neuman, Marcel Dekker, Inc. (1969). Suitable 1,2-cyclic ethers are the aromatic and polymeric types of epoxides. They can be aliphatic, cycloaliphatic, aromatic, or heterocyclic and will typically have an epoxy equivalency of from 1 to 6, preferably 1 to 3. Particularly useful are the aliphatic, cycloaliphatic, and glycidyl ether type 1,2-epoxides such as propylene oxide, epichlorohydrin, styrene oxide, vinylcyclohexene oxide, vinylcyclohexene dioxide, glycidol, butadiene oxide, glycidyl methacrylate, glycidyl ether of bisphenol A, 3,4-epoxycyclohexylmethyl-1,4-epoxycyclohexanecarboxylate, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexylmethyladipate, 3,4-epoxy-6-methylcyclohexylmethyladipate, diglycidyl ether of bisphenol A, epoxidized polybutadiene, 1,6-bis(oxazolidinyl) ether, polyglycidyl ether of phenylmethanediol, novolac resins, novolac phenolformaldehyde resins or novolac resins, novolac diglycidyl ether, and epoxy alloxanes, e.g., dimethylalloxanes having cycloaliphatic epoxide or glycidyl ether groups. A wider variety of commercial epoxy resins are available and listed in "Handbook of Epoxy Resins" by Lee and Neville, McGraw Hill Book Company, New York (1967) and in "Epoxy Resin Technology" by F. F. Brivies, John Wiley & Sons, New York (1968). Representative of the 1,3- and 1,4-cyclic ethers which can be polymerized in accordance with this invention are oxetane, 3,3-bis(calcaromethyl)oxetane, and tetrahydrofuran.

Another useful class of cationically-sensitive monomers which can be polymerized in accordance with this invention is represented by the general formula:

hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, phenylheptamethylcyclotetrasiloxane, vinylheptamethylcyclotetrasiloxane, methacryloyloxyethylheptamethylcyclotetrasiloxane, 2-bromomethylheptamethylcyclotetrasiloxane, 3-chloropropylheptamethylcyclotetrasiloxane, 1,2,3-tri(1,3,3-trifluoropropyl)trimethylcyclotrisiloxane, acetoxyethylheptamethylcyclotetrasiloxane, cyanoethylheptamethylcyclotetrasiloxane, 1,2,3-trihydroxyethylheptamethylcyclotetrasiloxane, and chlorobutylheptamethylcyclotetrasiloxane. Other known cyclic siloxanes are listed in "Chemistry and Technology of Silicones" by Walter Moll, Academic Press, New York (1966), Tables 41, 44 and 45.

The cyclic siloxanes can also be polymerized in the presence of relatively low molecular weight linear siloxanes such as hexamethyldisiloxane, chloropentamethyldisiloxane and octamethyltrisiloxane which serve to catalyze the growing chain and provide stable fluids or fluids having reactive end groups.

There is a host of commercially available:

20 cationically-sensitive monomers which can be used in this invention. In particular, cyclic ethers which are readily available include propylene oxide, oxetane, epichlorohydrin, tetrahydrofuran, styrene oxide, vinylcyclohexene oxide, glycidol, glycidyl methacrylate, acetylene oxide, phenyl glycidyl ether, 1,2-butene oxide, diglycidyl ether of bisphenol A (e.g., "Epon 828" and "DER 311"), vinylcyclohexene chloride (e.g., "CEL-4206"), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (e.g., "CEL-4221"), 3,4-epoxy-6-methylcyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate (e.g., "CEL-4201"), bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate (e.g., "CEL-4209"), aliphatic epoxy modified with polypropylene glycol (e.g., "CEL-4050" and "CEL-1051"), dipentene chloride (e.g., "CEL-4269"), epoxidized polybutadiene (e.g., "Celron 2061"), silicone epoxy (e.g., "Epi-Kem 90"), 1,4-butanediol diglycidyl ether (e.g., "Araldite 80-2"), polyglycidyl ether of phenolformaldehyde novolac (e.g., "DER-431").

"Epi-Kem 5/1" and "DER-438"), resorcinol diglycidyl ether (e.g., "Koponite"), polyglycol diepoxide (e.g., "DER 736"), polyacrylate epoxide (e.g., "Epoxy U-14"), urethane modified epoxide (e.g., "Q3599"), polyfunctional flexible epoxides (e.g., "Flexibilizer 151"), and mixtures thereof as well as mixtures thereof with co-curing agents, curing agents, or hardeners which also are well known (see Lee and Neville and Bruins, *supra*). Representative of the co-curing agents of hardeners which can be used are acid anhydrides, active of hardeners such as nadic methyl anhydride, cyclopentanetetracarboxylic dianhydride, pyromellitic anhydride, cis-1,2-cyclohexanedicarboxylic anhydride, and mixtures thereof.

In general, the polymerization of cationically-sensitive monomers with the ionic salt of an organometallic complex can be carried out at room temperature for the majority of cationically-sensitive monomers, although low temperature (e.g., -10°C) or elevated temperatures (e.g., 30° to 200°C, preferably 50° to 150°C), can be used to either subdue the exotherm of polymerization or to accelerate the polymerization. In the case of latent salt catalysts of this invention, temperatures generally in the range of 50° to 250°C, preferably from 50° to 150°C, can be used. The temperature of polymerization and amount of catalyst will vary and be dependent on the particular cationically-sensitive monomer used and the desired application of the polymerized or cured product. The amount of ionic salt of an organometallic complex to be used as a catalyst in this invention should be sufficient to effect polymerization of the cationically-sensitive monomer (i.e., a catalytically effective amount) under the desired use conditions. Such amount generally will be in the range of about 0.01 to 20 weight percent, preferably 0.5 to 5.0 weight percent, and most preferably 1.0 to 2.0 weight percent, based on the weight of cationically-sensitive monomer.

Solvents can be used to assist in dissolution of the ionic salt in the cationically-sensitive material and

are preferred for use in the polymerizable compositions.

Representative solvents include acetone, methyl ethyl ketone, cyclopentanone, methyl cellosolve acetate, methylene chloride, nitromethane, methylformate, acetoneitrile, and 1,2-dimethoxyethane (glyme).

The curable or polymerizable compositions of this invention comprising the cationically-sensitive monomer(s) and the ionic salt of an organometallic complex as catalyst can be used for applications such as those in which other cationically-sensitive compositions employing Lewis acid catalysts such as BF<sub>3</sub> or B<sub>2</sub>O<sub>3</sub> diethyl ether or the radiation sensitive onium salts are used. Thus, the compositions can be used as adhesives, caulking and sealing compounds, coating and molding compounds, potting and encapsulating compounds, impregnating and coating compounds, etc.

Depending on the particular cationically-sensitive monomer and ionic organometallic complex used. In addition, the composition may contain adjuncts (e.g., fillers, such as silicon, talc, glass bubbles, clay, reinforcing fibers, dyes, pigments, plasticizers, slip agents, antioxidants, surface modifying agents, etc.) as long as they do not interfere with the polymerization of the cationically-sensitive components of the composition or, where the ionic salt of the organometallic complex is radiation-sensitive, absorb radiation to which the complex is responsive.

For these compositions of the invention which are radiation-sensitive, i.e., the compositions containing cationically-sensitive monomers and an ionic salt of an organometallic complex of formulas I, II, and III, any source of radiation emitting active radiation in the ultraviolet and visible region of the spectrum (e.g., about 200 to 600nm) can be used. Suitable sources of radiation include mercury vapor discharge lamps, carbon arcs, tungsten lamps, neon lamps, sunlight, etc. The required amount of exposure to effect polymerization is dependent upon such factors as the identity and concentration of the organometallic ionic complex, the particular cationically-

sensitive monomer, the thickness of the exposed material, type of substrate, intensity of the radiation source and amount of heat associated with the radiation. Optionally, it is within the scope of this invention to include spectral sensitizers in the radiation-sensitive composition.

Any photosensitizer may be useful if its triplet energy is at least 45 kcal/mole. Examples of such sensitizers are given in Table 2-1 of the reference, Steven L. Murrov, Handbook of Photochemistry, Marcel Dekker Inc., NY, 27-35 (1973), and include pyrene, fluoroanthrene, benzil, chrysene, p-terphenyl, acenaphthene, naphthalene, phenanthrene, and biphenyl. When present, the amount of sensitizer used in the practice of the present invention is generally in the range of 0.01 to 10 parts, and preferably 0.1 to 1.0 parts, by weight of sensitizer per part of organometallic salt.

The objects and advantages of this invention are further illustrated by the following examples, many of which utilize as cationically-sensitive monomer a stock solution consisting of 1 part by weight of vinylcyclohexene dioxide and 1 part by weight of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate. The particular materials and amounts thereof recited in these examples, which are in parts by weight, as well as other conditions and details should not be construed to unduly limit this invention.

#### EXAMPLES 1-4

Polymerizable solutions were prepared by mixing in four suitable vessels 10 parts of stock solution, 1.0 part of acetoneitrile, and 0.1 part in each vessel respectively, of (Example 1) the hexafluoroantimonate, (Example 2) the hexafluoroarsenate, (Example 3) the hexafluorophosphate, and (Example 4) the tetrafluoroborate salt of (4-mesitylene)(3-cyclopentadienyl)iron(1+) (each prepared as described in W. A. Hendrickson, Ph.D. thesis, U. of Florida (1978)). The solutions were coated onto polyvinylidene chloride primed 7% micrometer polyester using a number 22 wire wound coating rod and the coatings allowed

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to air dry for 30 minutes. The coated samples were then exposed to a 150 watt tungsten spotlight at a distance of 10 cm from the sample surface. The time required to produce a non-tacky surface for each sample is given in Table I.

TABLE I

Ex. No.	Counterion of (n <sup>6</sup> -mesitylene)(n <sup>5</sup> -cyclopentadienyl)-	Time to produce non-tacky surface
1	iron(1+)	30 sec
2	SbF <sub>6</sub> <sup>-</sup>	30 sec
3	AsF <sub>6</sub> <sup>-</sup>	45 sec
4	PF <sub>6</sub> <sup>-</sup>	120 sec
	BF <sub>4</sub> <sup>-</sup>	greater than 30 min(a)

(a) becomes non-tacky after heating at 100°C for 60 min.

## EXAMPLES 5-7

Coatings were prepared as described in Examples 1-4 using as catalyst the hexafluorophosphate salts of, respectively, (Example 5) (n<sup>6</sup>-naphthalene)(n<sup>5</sup>-cyclopentadienyl)iron(1+), (Example 6) (n<sup>6</sup>-chrysene)(n<sup>5</sup>-cyclopentadienyl)iron(1+), and (Example 7) (n<sup>6</sup>-pyrene)(n<sup>5</sup>-cyclopentadienyl)iron(1+). (These salts were prepared according to the procedure described in J. Organometal. Chem. 101, 221 (1975)). Samples of each coating (labeled (b)) were exposed to the output of the 150 watt tungsten lamp as described in Examples 1-4 and other samples of the coatings (labeled (c)) were exposed to the output of the 150 watt tungsten lamp that passed through a light filter that removed 99% of the radiation below 440 nm. The time to produce a non-tacky coating for each sample is recorded in Table II.

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TABLE II

Ex. No.	Catalyst	Time to produce non-tacky surface
5	hexafluorophosphate salt of: (n <sup>6</sup> -naphthalene)(n <sup>5</sup> -cyclopentadienyl)iron(1+)	no filter 440nm filter
		(b) (c)
		30 sec 60 sec
10	(n <sup>6</sup> -chrysene)(n <sup>5</sup> -cyclopentadienyl)iron(1+)	30 sec 60 sec
7	(n <sup>6</sup> -pyrene)(n <sup>5</sup> -cyclopentadienyl)iron(1+)	15 sec 30 sec

## EXAMPLES 8 and 9

The procedure of Example 5-7 was repeated using as catalyst the hexafluorophosphate salt and the hexafluoroantimonate salt of (n<sup>6</sup>-fluorene)(n<sup>5</sup>-cyclopentadienyl)iron(1+). The time required to produce a non-tacky surface with the hexafluorophosphate salt was 60 seconds for exposures without the filter and 120 seconds with the filter.

With the hexafluoroantimonate salt, exposures to produce a non-tacky surface were 30 and 60 seconds respectively.

The (n<sup>6</sup>-fluorene)(n<sup>5</sup>-cyclopentadienyl)iron(1+) salts were prepared as described in Hendrickson, Ph.D. thesis, Univ. of Florida (1978).

## EXAMPLES 10-15

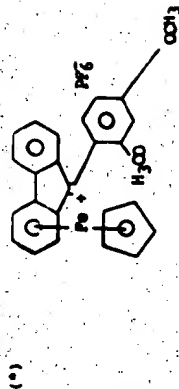
Coating solutions were prepared by mixing 10 parts of stock solution, 2 parts of acetone and 0.1 part of each of the various organometallic complex salts shown in Table III. Each solution was coated and dried as described in Examples 1-4 and exposed as described in Examples 5-7. The time required to produce a non-tacky surface for each is given in Table III.

TABLE III

Ex. No.	Catalyst (d), (e)	Time to produce non-tacky surface sec.	
		nc filter	440m filter
10	[(n <sup>6</sup> -1,2,3,4,4a,9a)-9-(4-methylphenyl)-methylidene]fluorene)-(n <sup>5</sup> -cyclopentadienyl)iron(1+)	30	90
11	[(n <sup>6</sup> -1,2,3,4,4a,9a)-9-(4-methoxyphenylmethylidene)fluorene)-(n <sup>5</sup> -cyclopentadienyl)iron(1+)	15	60
12	[(n <sup>6</sup> -1,2,3,4,4a,9a)-9-(2,4-dimethoxyphenylmethylidene)fluorene)-(n <sup>5</sup> -cyclopentadienyl)iron(1+)	30	60
13	[(n <sup>6</sup> -1,2,3,4,4a,9a)-9-(3,4-dimethoxyphenylmethylidene)fluorene)-(n <sup>5</sup> -cyclopentadienyl)iron(1+)	15	90
14	[(n <sup>6</sup> -1,2,3,4,4a,9a)-9-(3-phenyl-2-propenylidene)fluorene)-(n <sup>5</sup> -cyclopentadienyl)iron(1+)	60	90
15	[(n <sup>6</sup> -1,2,3,4,4a,9a)-9-(4-methyl-5-methylphenylmethylidene)fluorene)-(n <sup>5</sup> -cyclopentadienyl)iron(1+)	45	120

(d) All counterions are hexafluorophosphate

(e) Prepared by first condensing the corresponding aldehyde (i.e., 4-methylbenzaldehyde, 4-methoxybenzaldehyde, 2,4-dimethoxybenzaldehyde, 3,4-dimethoxybenzaldehyde, cinnamaldehyde, and 4-methyl-5-methylbenzaldehyde) with (n<sup>5</sup>-fluorene)(n<sup>5</sup>-cyclopentadienyl)iron(1+) hexafluorophosphate (prepared in Example 8) using a catalytic amount of potassium hydroxide in aqueous ethanol under nitrogen.



EXAMPLE 16

5 A coating solution, prepared by mixing 10 parts of stock solution, 1 part of acetonitrile and 0.1 part of (n<sup>6</sup>-toluene)(n<sup>5</sup>-cyclopentadienyl)iron(1+) hexafluorophosphate, (prepared as described in the previously cited Ph.D. Thesis of W. A. Hendrickson), was coated and dried as described in Examples 1-4. On exposure of the dried coating to a 150 watt tungsten spotlight at 10 cm, a non-tacky surface was obtained in 60 seconds. Only 30 seconds were required to produce a non-tacky surface when the coating was exposed to the output of a 275 watt G.E. 15 sunlamp at 10 cm.

EXAMPLES 17 AND 18

Example 16 was repeated using poly(n<sup>6</sup>-styrene)-(n<sup>5</sup>-cyclopentadienyl)iron(1+) hexafluorophosphate or poly-(n<sup>6</sup>-styrene)tricarbonylmanganese(1+) hexafluorocarsenate in place of (n<sup>6</sup>-toluene)(n<sup>5</sup>-cyclopentadienyl)iron(1+) hexafluorophosphate. Exposure times were 120 seconds and 45 seconds to produce a non-tacky coating using the 150 watt tungsten spotlight and the 275 watt sunlamp respectively.

25 The polystyrene iron complex was prepared as described in the before-mentioned Ph.D. thesis and the polystyrene manganese complex was prepared as described in J. Chem. Soc. (Chem. Comm.) 688 (1972) using polystyrene having a number average molecular weight of 22,000 in place of mesitylene or toluene, respectively. The iron complex

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obtained had approximately one ( $n^5$ -cyclopentadienyl)iron-(1+) unit per eight styrene units and the manganese complex obtained had approximately one tricarbonylmanganese(1+) unit per three styrene units.

## EXAMPLES 19-31

Polymerizable solutions were prepared as described in previous examples using the polymerizable compositions and the organometallic salts listed in Table IV. Each solution was coated onto primed polyester film and the coating dried as previously described, and exposed to polymerizing conditions as shown in Table IV. The time required to obtain a tack-free coating for each is given in Table IV.

TABLE IV

Ex.	NO.	Ionic organometallic complex salt (f)	Time of		Cure at 75°C
			min	sec	
15	19	(h) [(n <sup>5</sup> -1,2,3,4,8a,9a)(n <sup>5</sup> -5,6,7,8,8a,9a)cyclopentadienyl]bis(n <sup>5</sup> -cyclopentadienyl)diiron(2+)	15	sec	
		hexafluorophosphate			
20	20	(i) bis(n <sup>5</sup> -methylene)iron(2+)	greater than		
		hexafluorophosphate	30 min		
21	21	(j) bis(n <sup>5</sup> -methylene)iron(2+)	greater than		
		hexafluorocarbonate	30 min		
25	22	(j) bis(n <sup>5</sup> -methylene)iron(2+)			
		hexafluorocarbonate	5 sec		10 min
23	23	(k) bis(n <sup>5</sup> -hexamethylbenzene)cobalt(2+)			
		hexafluorocarbonate/hydroxyphenylfluorinate	10 sec		10 min

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TABLE IV continued

Ex.	NO.	Ionic organometallic complex salt (f)	Time of		Cure at 75°C
			min	sec	
5	24	(l) bis(n <sup>6</sup> -benzene)chromium(1+)			
		hexafluorocarbonate	20 sec		
25	25	(m) (n <sup>5</sup> -allyl)(n <sup>5</sup> -methylcyclopentadienyl)dicarbonylmanganese(1+) hexafluoroacetate	15	min	
10	26	(n) (n <sup>5</sup> -allyl)(n <sup>5</sup> -methylcyclopentadienyl)dicarbonylmanganese(1+) hexafluorophosphate	30	min	
27	27	(n) (n <sup>5</sup> -cycloheptatrienyl)tricarbonyliron(1+)	120	sec	30 min
		hexafluorocarbonate			
15	28	(o) (n <sup>5</sup> -cycloheptatrienyl)tricarbonylchromium(1+) hexafluorophosphate	15	min	
29	29	(o) (n <sup>5</sup> -cycloheptatrienyl)tricarbonylchromium(1+) hexafluorocarbonate	30	sec	
30	30	(o) (n <sup>5</sup> -cycloheptatrienyl)tricarbonylchromium(1+) hexafluorocarbonate	15	sec	
20	31	(o) (n <sup>5</sup> -cycloheptatrienyl)tricarbonylmolybdenum(1+) hexafluorocarbonate	30	sec	
32	32	(o) (n <sup>5</sup> -cycloheptatrienyl)tricarbonyltungsten(1+) hexafluorocarbonate	15	min	
25	33	(p) (n <sup>6</sup> -toluene)tricarbonylmanganese(1+)	10	sec	
		hexafluorophosphate			

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TABLE IV continued

Ex. no.	Ionic organometallic complex salt (f)	Time of analysis (g)	
		Oven at 75°C	
34	(p) (n <sup>6</sup> -cyclopentadienyl)iron(1+)	15 sec	
5	hexafluoroarsenate		
35	(q) (n <sup>6</sup> -methylcyclopentadienyl)iron(1+)	15 sec	
	hexafluoroarsenate		
36	(r) (n <sup>5</sup> -cyclopentadienyl)dicarbonyl- triphenylphosphineiron(1+)	240 sec	
10	hexafluoroarsenate		
37	(s) (n <sup>5</sup> -cyclopentadienyl)dicarbonyl- triphenylphosphineiron(1+)	45 sec	
	hexafluoroarsenate		
38	(r) (n <sup>5</sup> -cyclopentadienyl)dicarbonyl- triphenylphosphineiron(1+)	45 sec	
15	hexafluoroarsenate		
39	(r) (n <sup>5</sup> -cyclopentadienyl)dicarbonyl- triphenylacetyleneiron(1+)	10 sec	
	hexafluoroarsenate		
40	(r) (n <sup>5</sup> -cyclopentadienyl)dicarbonyl- triphenylacetyleneiron(1+)	5 sec	
	hexafluoroarsenate		
41	(r) (n <sup>5</sup> -cyclopentadienyl)dicarbonyl- triphenylacetyleneiron(1+)	10 sec	
25	hexafluoroarsenate		
42	(r) (n <sup>5</sup> -cyclopentadienyl)dicarbonyl- triphenylacetyleneiron(1+)	45 sec	
	phosphine		

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TABLE IV continued

Ex. no.	Ionic organometallic complex salt (f)	Time of analysis (g)	
		Oven at 75°C	
43	(t) (n <sup>5</sup> -cyclopentadienyl)dicarbonyl- triphenylacetyleneiron(1+)	greater than 60 min	
5	borate		
44	(s) hexacarbonylrhenium(1+)	20 sec	
	fluorantimonate/hydrogenhexafluoro- antimonate		
45	(s) (n <sup>5</sup> -cyclopentadienyl)tricarbonyl- iron(1+)	10 sec	30 min
10	hexafluoroarsenate		
46	(t) (n <sup>5</sup> -methylcyclopentadienyl)dicar- bonylnitrogen/hydrogen(1+)	30 sec	30 min
	phosphate		
47	(t) (n <sup>5</sup> -methylcyclopentadienyl)dicar- bonylnitrogen/hydrogen(1+)	15 sec	10 min
15	antimonate		
48	(u) (n <sup>6</sup> -antillene) (n <sup>5</sup> -cyclopentadienyl)iron- (1+)	15 sec	
	hexafluoroarsenate		
49	(u) (n <sup>6</sup> -antillene) (n <sup>5</sup> -cyclopentadienyl)iron- (1+)	15 sec	
	hexafluoroarsenate		
50	(u) (n <sup>6</sup> -antillene) (n <sup>5</sup> -cyclopentadienyl)iron- (1+)	15 sec	
	hexafluoroarsenate		
51	(v) [Cr(n <sup>6</sup> -benzenesulfate)dicarbonyl]- (1+)	120 sec	
25	hexafluoroarsenate		

(c) Coatings were made as described in previous examples using by weight 0.1 part of the ionic complex in a mixture of 5 parts of vinyl cyclohexane diisocyanate, 5 parts of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, and 1 part of acetonitrile with the exception of Samples 19-21 in which 2 parts of acetonitrile were used and Samples 22 and 51 in which 2 parts of nitromethane were used.

(d) Sequences were made using a 275 watt G. E. sunlamp at a distance of 30 cm from the coating.

10 Prepared in accordance with the procedure outlined in

(a) *J. Organometallic Chem.* **18**, 265 (1960).

(b) *J. Chem. Soc. (Chem. Comm.)* 900 (1971).

(c) *J. Organometallic Chem.* **1**, 307 (1964).

(d) *Organometallics* **5**, 133 (1986).

15 (a) *J. Organometallic Chem.* **13**, 38 (1966).

(b) *J. Chem. Soc. (Chem. Comm.)* 211 (1961).

(c) *Angew. Chemie* **72**, 939 (1959).

(d) *Angew. Chem.* **3**, 1037 (1964).

(e) *J. Chem. Soc. (Chem. Comm.)* 608 (1975).

20 (a) *Angew. Chem.* **1**, 933 (1963).

(b) *J. Inorg. Nucl. Chem.* **1**, 165 (1955) and *Inorg. Chem.* **3**, 1177 (1966).

(c) *J. Am. Chem. Soc.* **99**, 4776 (1977).

(d) *Organometallics* **5**, 133 (1986).

(e) *J. A. M. Chem. Soc.* **92**, 4776 (1977).

(f) *J. A. M. Chem. Soc.* **92**, 4776 (1977).

(g) *J. A. M. Chem. Soc.* **92**, 4776 (1977).

#### EXAMPLES 52-63

To illustrate the range of concentrations of ionic salts of organometallic complexes effective for catalyzing the polymerization of cationically polymerizable compounds, solutions were prepared as described previously consisting of stock solution, solvent, and 10.0 to 0.01 percent by weight, based on total weight of stock solution, of ionic salt as shown in Table V. Each mixture was coated onto poly(vinylidene chloride) primed polyester sheeting, dried, and exposed to the radiation of a 275 watt G. E.

sunlamp at a distance of 10 cm until the coating was non-tacky to the touch. The results are given in Table V.

TABLE V

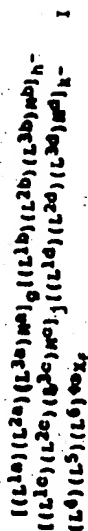
Ex.	No.	Ionic organometallic complex salt	Conc. of salt	Time of cure
5	52	bis( $\eta^6$ -mesitylene)iron(2+) hexafluoroantimonate	10.0	5 sec
10	53	bis( $\eta^6$ -mesitylene)iron(2+) hexafluoroantimonate	1.0	5 sec
15	54	bis( $\eta^6$ -mesitylene)iron(2+) hexafluoroantimonate	0.1	10 sec
20	55	bis( $\eta^6$ -mesitylene)iron(2+) hexafluoroantimonate	0.01	greater than 30 min
25	56	( $\eta^5$ -cyclopentadienyl)dicyarbonyl-triphenylstiboliron(1+) hexafluoroantimonate	10.0	5 sec
30	57	( $\eta^5$ -cyclopentadienyl)dicyarbonyl-triphenylstiboliron(1+) hexafluoroantimonate	1.0	5 sec
35	58	( $\eta^5$ -cyclopentadienyl)dicyarbonyl-triphenylstiboliron(1+) hexafluoroantimonate	0.1	45 sec
40	59	( $\eta^5$ -cyclopentadienyl)dicyarbonyl-triphenylstiboliron(1+) hexafluoroantimonate	0.01	greater than 30 min
45	60	( $\eta^6$ -mesitylene)( $\eta^5$ -cyclopentadienyl)iron(1+) hexafluoroantimonate	0.0	5 sec

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CLAIMS:

1. An energy polymerizable composition comprising a cationically polymerizable material and a catalytically effective amount of an ionic salt of an organometallic complex cation capable of adding an intermediate strength nucleophile or upon photolysis capable of liberating at least one coordination site, said metal in said organometallic complex cation being selected from elements of Periodic Groups IVA, VA, VIA, VIIA, and VIIIA.

2. The composition according to Claim 1 wherein said ionic salt has a formula selected from Formulas I, II, and III:



wherein  $M^a$ ,  $M^b$ ,  $M^c$ , and  $M^d$  each represents a metal selected from the elements of Periodic Groups IVA, VA, VIA, VIIA, and VIIIA;

with the proviso that Formula I can represent a mono-nuclear, binuclear, trinuclear, or tetranuclear complex compound comprising  $M^a$ ,  $M^b$ ,  $M^c$ ,  $M^d$ , or  $M^e$  respectively with their attendant ligands,  $L1$ ,  $L2$ ,  $L3$ ,  $L4$ , and  $L5$  each represents none, 1, 2, or 3

ligands contributing  $\pi$ -electrons that can be the same or different ligands selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of contributing two to twelve  $\pi$ -electrons to the valence shell of  $M^a$ ,  $M^b$ ,  $M^c$ , and  $M^d$  respectively;

$L2a$ ,  $L2b$ ,  $L2c$  and  $L2d$  each represents none or 1 to 6 ligands contributing an even number of  $\sigma$ -electrons

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TABLE V continued

No.	Ionic organometallic complex salt	Conc. of		Time of
		salt	ure	
1	$(\eta^5\text{-indenyl})_2(\eta^5\text{-cyclopentadienyl})\text{Ir}(\text{dppf})^+$	1.0	5 sec	
2	$(\eta^5\text{-indenyl})_2(\eta^5\text{-cyclopentadienyl})\text{Ir}(\text{dppf})^+$	0.1	30 sec	
3	$(\eta^5\text{-indenyl})_2(\eta^5\text{-cyclopentadienyl})\text{Ir}(\text{dppf})^+$	0.01	greater than 30 min	

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiment set forth herein.

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that can be the same or different selected from mono-, di-, and tri-dentate ligand-, each contributing 2, 4, or 6 e-electrons to the valence shell of  $M^0$ ,  $M^1$ ,  $M^2$ , and  $M^3$  respectively;

5  $L^0$ ,  $L^1$ ,  $L^2$ ,  $L^3$ , and  $L^4$  each represents none, 1 or 2 ligands contributing one e-electron each to the valence shell of  $M^0$ ,  $M^1$ ,  $M^2$ , and  $M^3$  respectively;

10  $L^5$  represents none or 1 to 6 bridging ligands containing e-electrons that can be the same or different ligand selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of acting as a bridging ligand contributing 2 to 24

15 e-electrons to the valence shells of two or more metal atoms  $M^0$ ,  $M^1$ ,  $M^2$ , or  $M^3$  simultaneously;

20  $L^6$  represents none or 1 to 12 bridging ligands contributing an even number of e-electrons that can be the same or different selected from mono, di, and tri-dentate ligands, each donating 2, 4, or 6 e-electrons to the valence shells of two or more metal atoms  $M^0$ ,  $M^1$ ,  $M^2$ , or  $M^3$  simultaneously;

25  $L^7$  represents none or 1 to 12 bridging ligands contributing 1, 2, 3, or 4 e-electrons to the valence shells of two or more metal atoms  $M^0$ ,  $M^1$ ,  $M^2$ , or  $M^3$  simultaneously;

with the proviso that the total electronic charge contributed to  $M^0$ ,  $M^1$ ,  $M^2$ , and  $M^3$  by the ligands  $L^0$ ,  $L^1$ ,  $L^2$ ,  $L^3$ ,  $L^4$ ,  $L^5$ ,  $L^6$ ,  $L^7$ ,  $L^8$ ,  $L^9$ ,  $L^{10}$ ,  $L^{11}$ ,  $L^{12}$ ,  $L^{13}$ ,  $L^{14}$ ,  $L^{15}$ , and  $L^{16}$  plus the sum of ionic charge on  $M^0$ ,  $M^1$ ,  $M^2$ , and  $M^3$  results in a residual net positive charge of e to the complex;

30 e is an integer having a value of 1, 2, or 3, the residual electronic charge of the complex cation;

35 x is a halogen containing complex anion of a metal or metalloids;

40 f is an integer of 1 to 3, the number of complex anions required to neutralize the charge e on the complex cation, and

45 0, 1, 2, and 3 independently are 0 or 1, with at least one

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of them being equal to 1;

$((L^7)(L^8)M^0)^+x_1$

II

wherein

5  $M^0$  represents a metal selected from elements of the Periodic Groups IVB, VB, VIB, VIIA, VIIIB, and VIIIIB;  
 $L^7$  represents none, one, or two e-electron contributing ligands that can be the same or different ligand selected from substituted and unsubstituted acyclic and allycyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic and heterocyclic aromatic compounds, each capable of contributing two to twelve e-electrons to the valence shell of  $M^0$ ;

10  $L^8$  represents none or 1 to 6 ligands that can be the same or different ligand selected from mono-, di-, and tri-dentate ligands, each contributing 2, 4, or 6 e-electrons to the valence shell of  $M^0$ ;

15 with the proviso that the total electronic charge contributed to  $M^0$  by  $L^7$  and  $L^8$  plus the ionic charge on  $M^0$  results in a residual net positive charge of e to the complex; and  
 20 e, x and f are as defined above; and

$((L^9)(L^{10})M^1)^+x_2$

III

wherein

25  $M^1$  represents a metal selected from Cr, Mo, W, Mn, Re, Ru, Rh, and Co;

30  $L^9$  represents one or two e-electron contributing ligands that can be the same or different ligand selected from substituted and unsubstituted  $\eta^5$ -allyl,  $\eta^5$ -cyclopentadienyl, and  $\eta^7$ -cycloheptatrienyl and  $\eta^6$ -aromatic compounds selected from  $\eta^6$ -benzene and substituted  $\eta^6$ -benzene compounds and compounds having 2 to 4 fused rings each capable of contributing 1 to 12 e-electrons to the valence shell of  $M^1$ ;

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L10 represents one, 1 to 3  $\pi$ -electrons contributing two  $\pi$ -electrons to the valence shell of  $M^p$ , with the proviso that the total electronic charge contributed to  $M^p$  by ligands L9 and L10, plus the ionic charge on  $M^p$  results in a residual net positive charge of  $q$  on the complex.

$q$  is an integer having a value of 1 or 2, the residual electronic charge of the complex cation;  $T$  is a halogen containing complex anion selected from  $AsF_6^-$ ,  $SbF_6^-$ , and  $Bu_4G^-$ , and

$a$  is an integer of 1 or 2, the number of complex anions required to neutralize the charge  $q$  on the complex cation.

3. The composition according to claim 2 wherein in Formula 1, the ligands L1a, L1b, L1c, and L1d of the 10 ionic salt

each contains less than 100 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, tellurium, antimony, germanium, tin, and boron;

20 the ligands L2a, L2b, L2c, and L2d of the ionic salt each is selected from

a. monodentate ligands having up to 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, and germanium; and

b. polydentate ligands capable of forming with metal  $M^p$ ,  $M^p$ ,  $M^p$ , or  $M^p$  a 4-, 5-, or 6-membered saturated or unsaturated ring containing up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, in addition to the metal atom

the ligands L3a, L3b, L3c, and L3d of the ionic salt each has up to 30 carbon atoms and up to 10 hetero atoms

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selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron;

the bridging ligand L4 of the ionic salt contains less than 100 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen and nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron;

the bridging ligand L5 of the ionic salt contains up to 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, and boron; and

the bridging radical L6 of the ionic salt has up to 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron;

wherein, in formula II

ligand L7 of the ionic salt contains less than 100 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron;

ligand L8 of the ionic salt is selected from:

a. monodentate ligands having up to 30 carbon atoms and up to 2 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron, and

b. polydentate ligands capable of forming with metal  $M^p$  a 4-, 5-, or 6-membered saturated or unsaturated ring containing up to 10 hetero atoms

selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron in addition to the metal atom; and

5 wherein, in Formula III

ligand L<sub>10</sub> of the ionic salt is selected from carbon monoxide and the nitrosonium ion, and  
ligand L<sub>9</sub> of the ionic salt contains up to 24 carbon and up to two heteroatoms selected from nitrogen, oxygen, and sulfur.

4. The composition according to claims 2 and 3 wherein the ligands L<sub>1a</sub>, L<sub>1b</sub>, L<sub>1c</sub>, and L<sub>1d</sub> each is independently unsubstituted or substituted by a group selected from hydrocarbyl, hydrocarbyloxy,

15 hydrocarbylmercapto, hydrocarbyloxyhydrocarbyl, hydrocarbylcarbonyl, hydrocarbylcarbonamido, phenyl, alko, boryl, halo, hydroxy, cyano, nitro, nitroso, oxo, dimethylamino, diphenylphosphino, trimethylsiloxy, and condensed rings, said group containing up to 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron, and

wherein the ligand L<sub>7</sub> or L<sub>9</sub> is substituted by a group selected from hydrocarbyl, hydrocarbyloxy, hydrocarbylmercapto, hydrocarbyloxyhydrocarbyl, hydrocarbylcarbonyl, hydrocarbylcarbonamido, phenyl, alko, boryl, halo, hydroxy, cyano, nitro, nitroso, oxo, dimethylamino, diphenylphosphino, trimethylsiloxy, and condensed rings, said group containing up to 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron.

5. The composition according to any preceding claim wherein said polymerizable material is selected from an epoxy group containing material, 1,2-1,3-, and 1,4-epoxide ethers (also designated as 1,2-, 1,3-, and 1,4-epoxides), vinyl ethers,  $\pi$ -vinyl compounds, ethylenically-unsaturated hydrocarbons, cyclic formals, and cyclic organosilanes.

6. The composition according to any preceding claim wherein said salt is present in an amount in the range of 0.01 to 20 weight percent of said essentially polymerizable material.

7. The composition according to any preceding claim further comprising in the range of 0.01 to 10 parts by weight of a spectral sensitizer per part of organometallic salt.

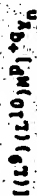
8. The composition according to claims 2 to 7 wherein said L<sub>1a</sub>, L<sub>1b</sub>, L<sub>1c</sub>, L<sub>1d</sub>, L<sub>2a</sub>, L<sub>2b</sub>, L<sub>2c</sub>, L<sub>2d</sub>, L<sub>3a</sub>, L<sub>3b</sub>, L<sub>3c</sub>, L<sub>3d</sub>, L<sub>4</sub>, L<sub>5</sub>, and L<sub>6</sub> ligands independently are groups on a polymeric chain.

9. A process for polymerizing the composition according to any preceding claim, said process comprising:  
a. admixing said essentially polymerizable material with a catalytically effective amount of said ionic salt of an organometallic complex, and  
b. curing the resulting admixture with a thermal or actinic radiation source.

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10. A compound according to Claims 2 to 7 having the formula:



wherein

5 M represents a metal selected from Cr, Mo, W, Mn, Re, Fe, and Co;

L<sup>9</sup> represents 1 or 2 ligands contributing s-electrons that can be the same or different ligand selected from substituted and unsubstituted s<sup>2</sup>-allyl, s<sup>2</sup>-cyclopentadienyl, and s<sup>2</sup>-cycloheptatrienyl and substituted

10 s<sup>2</sup>-aromatic compounds selected from s<sup>2</sup>-benzene and substituted s<sup>2</sup>-benzene compounds and compounds having 2 to 4 fused rings each capable of contributing 3 to 12 s-electrons to the valence shell of M;

15 L<sup>10</sup> represents none or 1 to 3 ligands contributing an even number of s-electrons that can be the same or different ligand selected from carbon monoxide or nitrosonium;

with the proviso that the total electronic charge contributed to M by L<sup>9</sup> and L<sup>10</sup> plus the ionic charge on metal M results in a net residual positive charge of q to the complex; and

q is an integer having a value of 1 or 2, the residual electrical charge of the complex cation;

25 Y is a halogen-containing complex anion selected from AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup> and BF<sub>4</sub>OH<sup>-</sup>; and

n is an integer having a value of 1 or 2, the number of complex anions required to neutralise the charge q on the complex cation.